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Routine Methods for the Determination of contents and Isotopic compositions of U and Pu in Nuclear Grade Oxides at PNC.

酸化物燃料のウランおよびプルトニウム含有率・同位体組成分析

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Routine Methods for the Determination of Contents and Isotopic Compositions of U and Pu in the Nuclear Grade Oxides at PNC.

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Sammary:

Outlines of the chemical analysis methods for the nuclear grade oxides now being used to the routine samples prepared for the quality assurance object or the SALE program samples were described. These contain analytical methods of uranium concentration by the NBL-Davies-Gray method, of plutonium concentration by the AgO/Fe(II) potentiometry, and of isotopic compositions of U and Pu by the surface ionization mass spectrometry.

Presented at SALE Program Meeting held on June 29 to July 1, 1976 at New Brunswick Laboratory, New Brunswick, N.J.,USA.

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酸化物燃料のウランおよびプルトニウム含有率・同位体組成分析について

技術部分析課　坪谷隆夫

要　旨　現在，動燃において定常分析およびSALE Program(Safeguards Analytical Laboratory Evaluation Program)に用いているDavies-Gray法によるウラン含有率分析法，$Ag\overline{O}$／Fe(Ⅱ)電位差摘定法によるプルトニウム含有率分析法，および表面電離化方式質量分析法によるウランとプルトニウム同位体組成分析法の概要を述べる。

I would like to present to you several chemical analysis methods that are used for the determinations of the content and of the isotopic composition of uranium and plutonium in reactor grade oxide fuels. Those methods are used in our section for the purpose of routine shipping/acceptance analysis and of the SALE program sample analysis.

(1st slide)
This is the flow sheet for the determination of uranium content in the oxides. RSDs are resulted 0.08% for U-NO_3 solution and 0.10% for the oxides using 100 mg of total U. We use metal uranium purified over 99.99%, JAERI-U4, as the primary standard.

As the literatures pointed out, we also experienced a negative bias if the end point potential was not attained within 5 mins. after 1M H_2SO_4 was added. Although dicromate titration was rapidly performed when the vanadyl concentration was increased, a positive bias was obtained.
(The condition shown in Figure: (U): 4.2×10^{-4} mole, (V): 2.5×10^{-4} mole)
(The oxidation-reduction related to this determination:

$$U(IV) + 2V(IV) \rightarrow U(VI) + 2V(III)$$
$$3V(III) + Cr(VI) \longrightarrow 3V(IV) + Cr(III)$$
$$3U(IV) + 2Cr(VI) \rightarrow 3U(VI) + 2Cr(VI))$$

We store the Pt electrode in 0.5M H_2SO_4 solution to maintain its surface in an activated state. This resulted in a sharp potential variation at the end point.

(2nd slide)
This is the flow diagram for the determination of plutonium content in the oxide fuels.
The plutonium valence is adjusted to hexavalence by silver nitrate and persulfate instead of adding silver as the peroxide.
Excess Ag(II) ion formed by the oxidation reaction of persulfate and excess persulfate are decomposed by heating the sample solution.
RSDs are 0.50% for PuO_2, $(Pu,U)O_2$, or Pu-NO_3 solution when a sample contained 20 to 40 mg of Pu.

(3rd slide)

We routinely use three sets of the same typed surface ionization mass spectrometers for the determination of isotopic compositions. The name of the machines is Nuclide 12.90SU2.

We also use a multichannel analyser system with Si-semiconductor detector for the α-spectrometry of Pu-238 and the other plutonium isotopes.

For mass spectrometry, a triple filament made of either rhenium or tungsten as the side filaments and of rhenium as the center filament is used.

The peak intensities from object isotopes are recorded on a strip chart cyclically by increasing and decreasing the current of the magnet field coil.

Each machine is able to determine two sample filaments and one NBS standard filament during one working day.

To increase a throughput of the sample processing, from three determinations per day to six to eight determinations and maintain satisfactory analytical quality, we are testing a filament degassing treatment system to degass a sample loaded filament independently of the mass spectrometer operations.

We are going to connect a 64 kbytes minicomputer having a disc device with the mass spectrometers and the other machines by the time shared basis. We expect the computer based mass spectrometers to enable us to eliminate time consuming manual handling by digitizing a lot of analog data on the strip chart.

Now, we degitalize the analog data by using a slide caliper, then process by computer programs written in FORTRAN IV for an IBM 360/195-G compiler time sharing system. Each program was coded as LEURAN for low enriched uranium, below 50 % of U-235,HEURAN for high enriched uranium, PLUTO for plutonium, and NDMS for neodymium. These programs calculate isotope ratios, standard deviations atom percents, and weight percents after statistical treatments such as the Dixon criterion were performed. They are also able to calculate the mass discrimination bias and to check accuracy.

This table shows an example of an accuracy check analysis used on NBS-SRM-948. Isotope ratios with a negative sign were outliers, and omitted from the data evaluation. PLUTO is able to combine mass spectrometric data with α-spectrometric data.

The certified values of NBS-SRM-948 are corrected to the up-dated values after the decay of Pu-238 and Pu-241 are calculated by inputting lapse periods.

The result of the accuracy check in that Table shows that observed values coincided fairly well with NBS values, so that we can decide a mass discrimination bias used in that calculation and all of the analytical conditions were good. We use natural noedymium for the mass discrimination bias measurement once every month, and the isotope ratio of ND-142 to Nd-150 is adopted 4.824(ASTM-E-321).

Figure 1 Determination of U content by a method similar to NBL-Davies-Gray method (slide 1st).

Figure 2 Determination of Pu content by an AgO/Fe(II) potentiometry (slide 2nd).

Table 1 An example of an accuracy check calculation using a computer code PLUTO (slide 3rd).

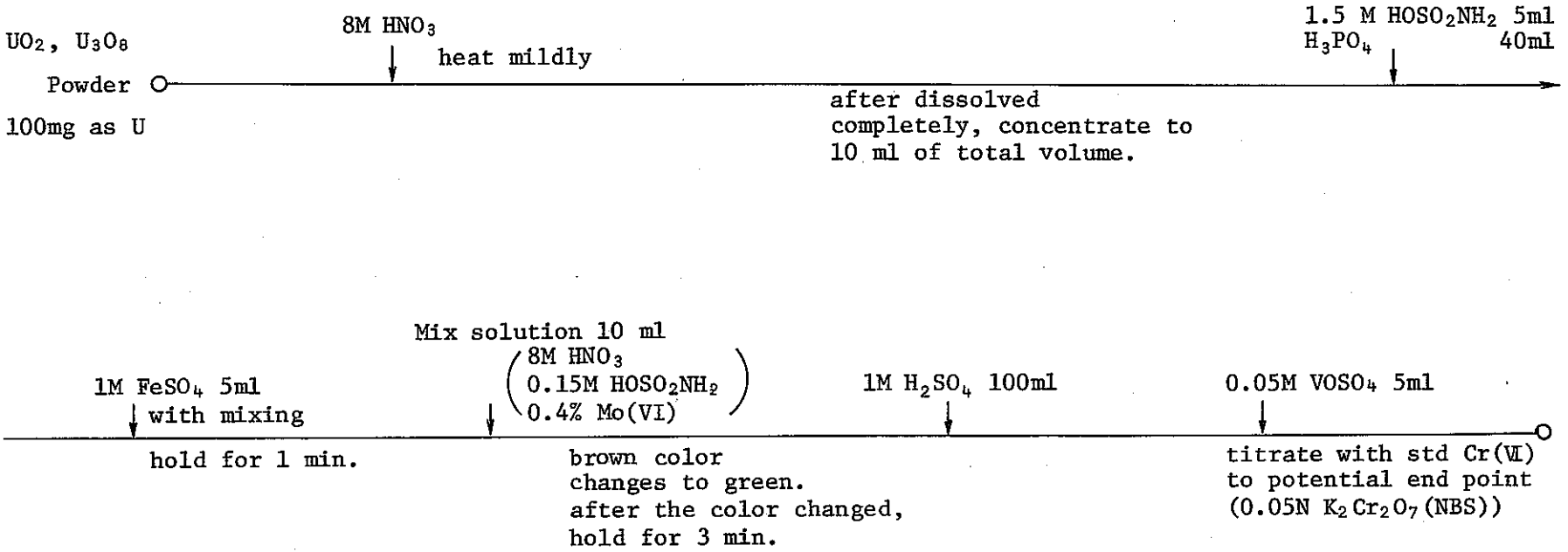

Figure 1. Determination of U content by a method similar to NBL-Davies-Gray method.

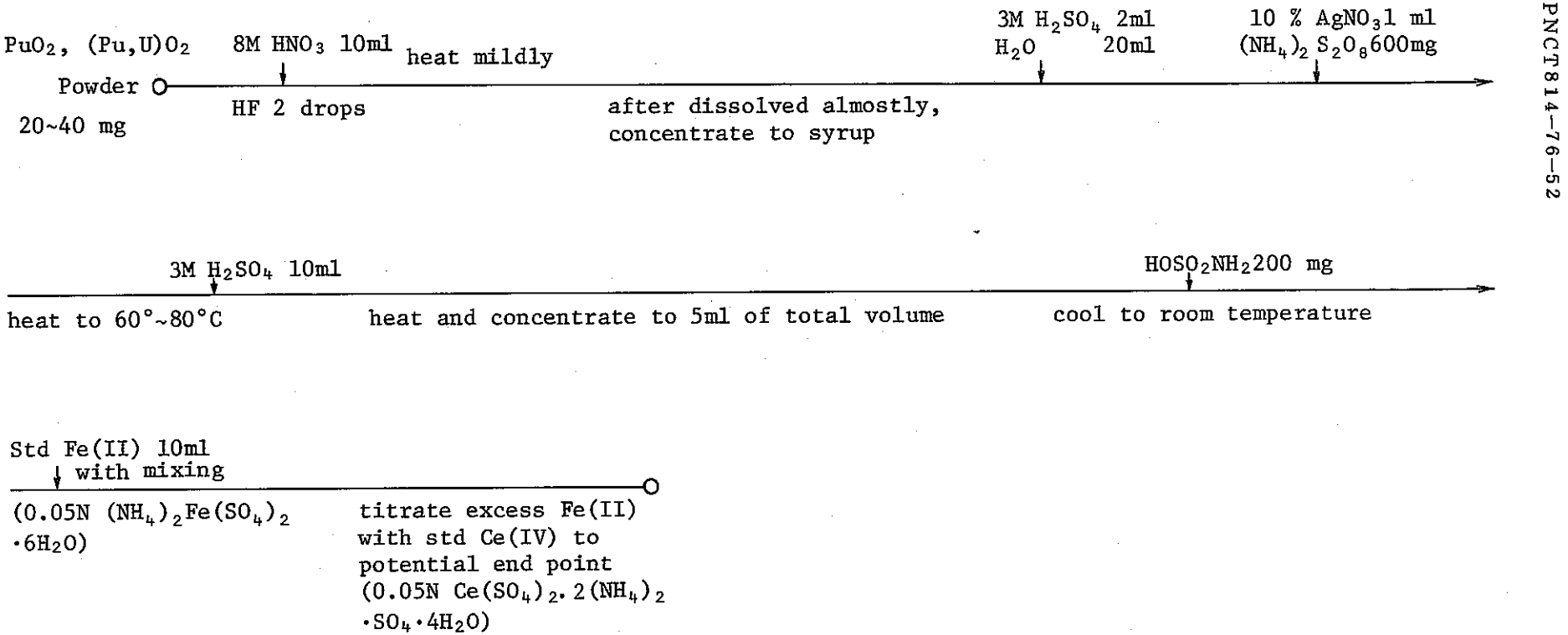

Figure 2. Determination of Pu content by an AgO/Fe(II) potentiometry.

Table 1 An example of an accuracy check calculation using a computer code PLUTO.

PLUTONIUM DOITAI SOKUTEI-SAMPLE MEI=(NBS948)

DATE OF ANALYZED=S51.5.21
APPARATUS = SU 2-9
ANALYST(S) = Y.KURAMIT
USER S CODE=

INPUT DATA BIAS=0.68019					OUTPUT DATA			
	PU239	PU240	PU241	PU242	R238/239	R240/239	R241/239	R242/239
V.R	10.00	1.00	0.10	0.03				
1	772	665	329	92	*	0.8614D - 01	0.4262D - 02	0.3575D - 03
2	780	671	330	91	*	0.8603D - 01	0.4231D - 02	0.3500D - 03
3	788	678	334	92	*	0.8604D - 01	0.4239D - 02	0.3503D - 03
4	794	681	336	94	*	0.8577D - 01	0.4232D - 02	0.3552D - 03
5	801	689	339	96	*	0.8602D - 01	0.4232D - 02	0.3596D - 03
6	806	695	342	99	*	0.8623D - 01	0.4243D - 02	0.3685D - 03
7	813	702	346	102	*	0.8635D - 01	0.4256D - 02	0.3764D - 03
8	823	709	350	103	*	0.8615D - 01	0.4253D - 02	0.3755D - 03
9	831	718	353	103	*	0.8640D - 01	0.4248D - 02	0.3718D - 03
10	840	724	356	104	*	0.8619D - 01	0.4238D - 02	0.3714D - 03
11	850	731	359	105	*	0.8600D - 01	0.4224D - 02	0.3706D - 03
12	859	736	364	107	*	0.8568D - 01	0.4237D - 02	0.3737D - 03
13	866	742	370	107	*	0.8568D - 01	0.4273D - 02	0.3707D - 03
14	874	756	373	108	*	0.8650D - 01	0.4268D - 02	0.3707D - 03
15	875	760	3790	105	*	0.8686D - 01	-0.4331D - 01	0.3600D - 03
16	883	765	380	105	*	0.8664D - 01	0.4304D - 02	0.3567D - 03
17	880	766	378	105	*	0.8705D - 01	0.4295D - 02	0.3580D - 03
18	882	758	375	114	*	0.8549D - 01	0.4252D - 02	0.3878D - 03
19	883	762	377	106	*	0.8630D - 01	0.4270D - 02	0.3601D - 03
20	874	753	376	95	*	0.8616D - 01	0.4302D - 02	-0.3261D - 03
21	871	752	374	100	*	0.8634D - 01	0.4294D - 02	0.3444D - 03

RESULT OF PHA
(REGION)

PU-238	PU-239
100762	3891883

(SCAN)				
HEIKINCHI	=	*	0.8621E - 01	0.6117E - 02	0.3626E - 03
SIGMA	=	*	0.3496E - 03	0.8523E - 02	0.1349E - 04
CV	=	*	0.4055E + 00	0.1393E + 03	0.3719E + 01
HEIKIN(DIX)=		*	0.8621E - 01	0.4258E - 02	0.3644E - 03
CV(DIX)	=	*	0 4055E + 00	0.5909E + 00	0.2977E + 01
KIKYAKU SU =		*	0	1	1
(MS.)--CALIBRATED DATA ON SINGLE MS. DETERMINATION					
RATIO	=	0.1235E-03	0.8646E - 01	0.4282E - 02	0.3676E - 03
SIGMA	=	0.1296E-05	0.7651E - 04	0.5658E - 05	0.2447E - 05

	ATOM %	WEIGHT %
PU238	0.01131+0.00023	0.01126+0.00023
239	91.63974+0.01264	91.60597+0.02134
240	7.92292+0.01379	7.95313+0.01392
241	0.39239+0.00102	0.39554+0.00103
242	0.03368+0.00044	0.03410+0.00044

MOLECULAR WEIGHT OF PU = 239.13814

+ MEANS 95 % CONFIDENCE LIMIT OF SINGLE MS. DETERMINATION

```
HEIKIN? IF YES, INPUT 5, NO, INPUT 0
?
0

ACCURACY CHECK O SURUKA? IF YES, INPUT 5, NO INPUT O
?
5

INPUT ATOM % OF NBS FROM PU238 TO PU242
?
0.011, 91.574, 7.914, 0.468, 0.033

INPUT KEIKA JIKAN(YEARS)--PU241 NO HOSEI
?
3.65

RESULT OF THE ACCURACY CHECK ABOUT ATOM PERCENT
       PU238     PU239     PU240     Pu241     Pu242 (%)
(NBS)  0.011      91.641    7.920     0.396     0.0330    KEIKA JIKAN = 0.365E + 01 YEAR(S)
       5.7885    - 0.0011  0.0398    -0.8477   1.9998
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